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Nanostructured Hydroxyapatite Coatings for Improved Adhesion and Corrosion Resistance for Medical Implants

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Abstract: Hydroxyapetite (HA) coating on medical implant has been used in commercial application for several decades. The coating, commercially made by thermal spray method, functions as a intermediate layer between human tissues and the metal implant. The coating can speed up early stage healing after operation but the life span is much limited by low interfacial bond strength, which comes from the dissolution of amorphous HA in human body fluid during its service. This amorphous phase is formed in coating process under high temperature. To overcome these problems, we have developed a novel room temperature electrophoretic deposition process to fabricate nanostructured HA coating. This nanostructured HA coating significantly improved coating's bond strength up to 50-60 MPa, 2-3 times better than the thermal sprayed HA coating. The nanostructured HA coating also has corrosion resistance 50-100 times higher than the conventional HA coating. X-ray diffraction shows that all the HA coating is fully crystalline phase. It is expected that the implants with the nanostructured HA coating will have much longer service life. Other benefits derived from this process include room temperature deposition, the ability to control the coating microstructure and phases, and low cost for production.

INTRODUCTION

The field of hydroxyapatite ("HA") coatings is growing very rapidly. Since the 1980's, titanium implants typically have been coated with HAP using thermal spray techniques. There are two major shortcomings associated with plasma-sprayed HAP coatings. First, due to the high temperature plasma (≥15,000°C), a large fraction of crystalline HAP turns amorphous while in transit. This phase is soluble in body fluids and results in subsequent dissolution of the material during operation. Second, while thermal spray coatings in general are characterized by strong mechanical bonds, on a relative scale, this type of bond is weak in comparison to metallurgical or chemical bonds. In the 1990's, a chemical precipitation method was used for coating porous implants. This process operated at a temperature lower than 100°C, overcoming the HA dissolution problem, but the bonding between the HA coating and substrate interface is very week. In fact, the *poor adhesion* of HA coatings to titanium substrates is *the* single most troublesome aspect of today's technologies in relation to the viability of commercial implantable products [1].

Free-standing crystalline nanostructured HA ("*n*-HA") has been synthesized by Ying *et al.* [2] using a wet chemical synthesis technique. Note that this material has not been fabricated as a coating. Powder agglomerates were consolidated into bulk form for testing of mechanical properties such as fracture toughness, and bend and compressive strength. The MIT group found that the compressive strength of bulk n-HA can be increased up to 4-fold in comparison to bone

(879 MPa *vs.* 193 MPa for compacted bone). The bend strength was found to be roughly equivalent (193 MPa *vs.* 160 MPa in bone). These impressive numbers are a good indication of what can be anticipated in electrophoretic n-HA.

Electrophoretic deposition of HA can be done at room temperature (or lower) and avoids problems related to formation of the amorphous phase. Most importantly, the nature of the bond is metallurgical rather than mechanical and is expected to result in dramatically improved bond strength in comparison to thermal spray techniques. In addition, electrophoresis enables multicomponent codeposition. However, one disadvantage is porosity, allowing body fluid to enter and cause corrosion of the titanium substrate, and delamination. High temperature sintering has been used to decrease porosity and increase the density to mitigate this problem. Unfortunately, due to a poor mismatch in thermal expansion coefficients between the HA and titanium at high temperatures (during sintering) and the large volume pore reduction, cracks result.

In contrast, for nanostructured materials, this has been found to be less of a problem [3]. It has been demonstrated that nano ceramics have thermal expansion coefficients that nearly match the metal alloys due to the large volume fraction of atoms located at the grain boundary, which improves mobility [3,4]. To date, electrophoretic deposition ("EPD") of HA has been limited to conventional materials of micron grain size [5-9]. Mechanical properties of the micron HA are limited by relatively poor bend strength, fracture toughness, and compressive strength. Also, n-HAP can be sintered at a much lower temperature, as has been demonstrated for n-TiO_2, which can be sintered at 1/3 of the melting point (600 °C vs 1400 °C) [4]. At lower temperatures, there is less thermal expansion. We expected that the n-HAP could be sintered at a much lower temperature (900 °C or lower with low pressure HIPing, 500 °C), as observed by Ying [2]. Finally, a dense gradient bond coat of TiO_2 was introduced (a few microns thick) between n-HAP and titanium, so that body fluids have no opportunity to attack and degrade the titanium substrate.

EXPERIMENTAL PROCEDURES

Nanostructured HA powders were synthesized using a wet chemical process. This wet chemical process produced high quality n-HA particles with particle size ranging from 20 to 50 nm. The as-synthesized n-HA particles were suspended in polarized solvent. Ti6Al4V coupons with 1.0 inch diameter and 0.25 inch thickness were used as a substrate. The Ti alloy and platinum were used as cathode and anode, respectively. This process produced tenacious HA nanocoatings.

Characterization of the HA nanocoatings included interfacial bond strength using ASTM Standard F 1501-95 via tensile tester, Surface and cross-sectional microstructure and morphology using SEM, in-vitro testing of the coated coupons in simulated human body fluids, and electropolarization measurements during in-vitro tests.

EXPERIMENTAL RESULTS AND DISCUSSION

Microstructure and bond strength: The EPD process produced a high quality HA nanocoating. Both surface and cross-sectional SEM indicated that the as-produced HA nanocoatings were highly dense with few closed pores. Fig. 1 shows a typical SEM cross-sectional view of the coating. The cross-section morphology showed a very clean coating to substrate interface and

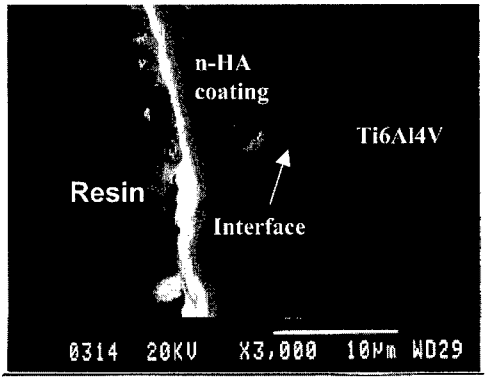

Fig. 1. SEM micrograph showing the cross-sectional view of nano-HA on Ti substrate. Note that the coating to substrate interface is clean, and with high bond strength.

high density. Coating to substrate adhesion evaluation using direct-pull-tests indicated that the as-fabricated nanocoatings exceed 60 MPa, exceeding the FDA required bond strength value, which is 50 MPa.

PH Change with time. Fig. 2 shows the pH change with soaking time in simulated human body fluid at 37 °C. In comparison, plasma sprayed conventional micrometer sized HA coatings were also tested using the same conditions. It was found that the EPD n-HA coatings kept a constant pH value at 6.5 soaked in the simulated body fluid for more than 60 days. However, in the case of plasma sprayed HA coatings, the simulated human body fluid had a sudden pH increase up to 9.7. Two days latter, the pH reached the highest point of 10.5. After that, the pH gradually went down to 7.5 and tended to be stable within 30 days. These curves demonstrated that the EPD coated n-HA coatings were much more stable than the conventional thermal sprayed HA coating during in-vitro tests in the simulated body fluid.

Calcium content change with time. Fig. 3 shows the calcium content change with soaking time of both conventional thermal sprayed ("T/S") HA coatings and EPD n-HA coatings. The calcium content release ranking can be expressed as

Non-heat treated T/S HA coating > heat treated T/S HA coating > EPD n-HA coatings

For the two thermal sprayed HA coatings, both exhibited high calcium release, which was caused by the dissolution of amorphous HA and other impurities of calcium phosphates of the coatings in the simulated human body fluid. In the actual experiments, we also found a white-colored

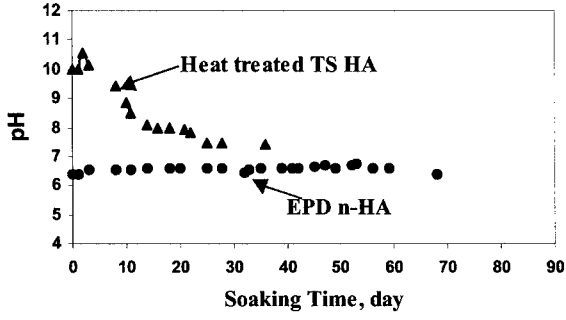

Fig. 2. pH plot vs. soaking time during in-vitro testing in the simulated human body fluid.

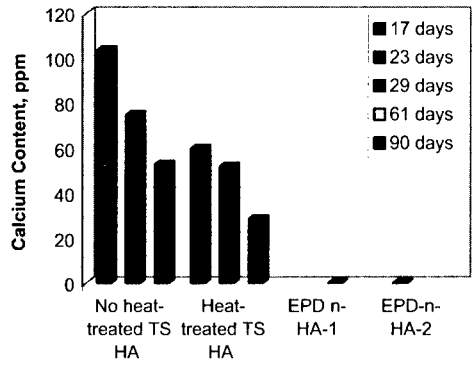

Fig. 3. Calcium content release into the simulated body fluid vs. different materials at 37°C for 3 months.

material, which first appeared on the thermal sprayed HA coating surface and then gradually dissolved into the solution. This phenomenon was more serious for the non-heat treated thermal sprayed HA coatings than for the heat-treated ones. It was noticed that calcium release of the thermal sprayed HA coatings decreased with the soaking time. For the heat-treated HA coating, the calcium content release was: 60.1, 52.2, and 28.8 ppm for soaking 17, 29, and 90 days in the simulated body fluid, respectively. The decrease of the calcium release could be explained by the reaction of the calcium ions with absorbed CO_2, which produces $CaCO_3$. When solid $CaCO_3$ formed, the Ca^{2+} concentration would decline. The CO_2 absorption and reaction with Ca^{2+} can explain pH gradually going down with soaking time in Fig. 2.

The most important finding was that, for both EPD nanocoatings, *e.g.,* n-HA-1 coatings soaked 61 days and EPD n-HA-2 for 23 days, the calcium contents in the simulated human body fluid were zero, indicating no calcium release to the simulated body fluid.

Electrochemical Corrosion: The corrosion resistance results for both EPD n-HA coatings and thermal sprayed HA coatings are shown in Fig. 4, where the n-HA coating had a corrosion current 50-100 time smaller than the thermal sprayed coating in simulated human body fluid at room temperature.

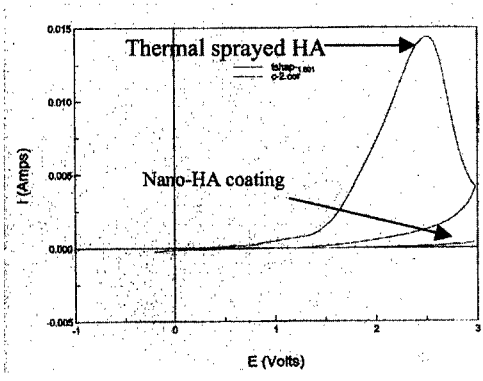

Fig. 4. Electro-polarization corrosion curves for both EDP n-HA coatings and thermal sprayed HA coatings.

As shown in Fig. 1, the n-HA coatings are nearly 100% dense. XRD analysis indicated 100% crystallinity of the HA nanocoatings. In the n-HA coatings, simulated human body fluid had no chance for contact with the Ti alloy surface, consequently, no corrosion occurred. In contrast, thermal sprayed HA coating had many defects associated with the as-fabricated coatings, porosity, and cracks were evident, as well as the presence of amorphous phases. The interfacial and coating cracks are usually formed during cooling down of the fabricated components in the thermal spray process, due to large thermal expansion coefficient differences between the HA coating (α_{HA}=13.5 $\times 10^{-6}$ /°C) and the Ti substrate (α_{Ti}=9.5 $\times 10^{-6}$ /°C).

The interfacial reaction at the interface area is divided into two steps. First, the H^+ produces at the interface area when corrosion occurs (eq. 1). Second, the HA material dissolves in the high H^+ concentration area (eq. 2). Because the H^+ cannot be well circulated out at interface, the local pH of the interface is extremely low. The HA dissolution automatically speeds up, so this corrosion is a self-catalytic process. Whenever the corrosion starts, it cannot stop until the entire interfacial HA material is dissolved. Since water can easily go through the connective cracks of the thermal sprayed coating, the corrosion proceeds very quickly. This is why conventional thermal sprayed HA coating always fails at the HA/Ti ally interfacial area.

$$Ti + 2H_2O = TiO_2 + 4H^+ + 4e \quad (1)$$

$$Ca_{10}(PO_4)_6(OH)_2 + 2H^+ = 10Ca^{2+} + 6(PO_4)^{-3} + H_2O \quad (2)$$

Bond strength changes with soaking time in-vitro: It is seen in Fig. 5 that the EPD n-HA coatings have much higher initial tensile bond strength (50-60 MPa) than that of conventional thermal sprayed HA (30 MPa) and chemical deposited HA coatings (14 MPa) before *in-vitro* corrosion in simulated human body fluid was conducted. During the *in-vitro* testing period, e.g., 10 weeks, the bond strength of the n-HA coatings kept a constant value (60 MPa), while the plasma sprayed and chemical deposited HA coatings have a significant bond strength loss.

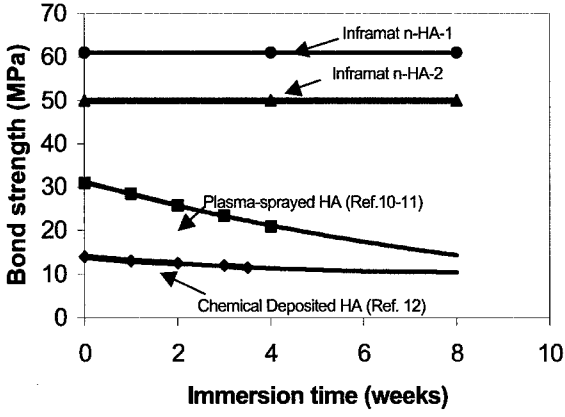

Fig. 5. Bond strength vs. soaking time during in-vitro test in simulated body fluid. The experimental errors are 10% of the data

CONCLUSIONS:

1. The EPD n-HA coating has strong interfacial bonding on Ti alloy and maintained tensile bond strength 50-60 MPa after 2 month in-vitro testing, which was much better than the plasma-sprayed HA and chemical precipitated HA coating that suffered bond strength loss in vitro.
2. The electrochemical corrosion resistance of the EPD n-HA coating was 50-100 times higher than the plasma-sprayed HA coating.
3. The EPD n-HA coating did not exhibit dissolution in simulated human body fluid in 2-month *in-vitro* test.

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